JULY 24, 1989

CHEMICAL & ENGINEERING

NEWS

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CHEMICAL & ENGINEERING
NEWS
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LETTERS

CHEMICAL SAFETY

Iodosobenzene salt explosion

SIR: Iodosobenzene tetrafluoroborate was described in 1988 by V. V. Zhdankin et al. [*Tetrahedron Lett.*, **29**, 3717 (1988)] as the first stable hypervalent iodine reagent without a nucleophilic ligand. After having prepared a few grams of the product according to the protocol in the cited literature without any difficulties, we decided to undertake a 0.5 mol preparation in the same manner. After drying the yellow crude product (about 75 g) in vacuo at room temperature for about 20 hours, it exploded while still in the flask in vacuo, producing a considerable amount of pungent fumes. The blast from the explosion was such that fragments of the flask penetrated glassware standing nearby as well as a security shield located in front of the flask. Fortunately, no one was in the laboratory at the time of the explosion.

We are unable to say whether the explosion was caused by impurities or by the instability of the product itself. However we would like to warn anyone preparing or handling iodosobenzene tetrafluoroborate to be extremely careful.

Gert van Look
Fluka Chemie A.G.
Buchs, Switzerland

Public image problem

SIR: The chemical industry has a public image problem nearly as serious as that of the nuclear power industry. Both industries produce harmful by-products (and in some cases, products) that are not always disposed of safely. An unwitting public has occasionally been exposed to dangerous levels of toxic wastes. This has tended to erode public trust in the industry and its spokesmen.

Unfortunately, the response of the chemical industry in general, and C&EN writers in particular, has often been a defensive, reflexive denial of the problem. To be sure, apocalyptic environmentalists are sometimes just as guilty of this unthinking, knee-jerk approach to chemistry (and science in general). But this is all the more reason to approach these problems rationally, admitting fault and proposing effective, timely solutions where appropriate. Here are two examples.

The first is John Weisburger's review of "In Search of Safety: Chemicals and Cancer Risk," by John Graham et al. (C&EN, May 22, page 35). For a page and a half Weisburger gives a lucid review of a well-written book analyzing the scientific, legal, and public policy aspects of regulating exposure to carcinogens. At the very end of the piece he adds his own personal opinion that since lifestyle factors (primarily smoking and nutrition) are responsible for 65 to 90% of cancer cases, the fight against cancer would be more effectively waged on the educational front (to alter lifestyles) than on the regulatory front. This pro-industry sentiment is prominently featured by the editors at the head of the article, even though it is presented as Weisburger's own opinion and not that of the authors of the reviewed book. I might add here that we are not forced to choose between education or regulation: We can and should do both. Lifestyle is voluntary, however, and cannot be regulated in a free society. Chemical exposure, which by Weisburger's lowest estimate causes 100,000 cancer cases annually, can and must be legally regulated.

Robert Hollingworth's review of "Pesticide Alert" by Laurie Mott and Karen Snyder (C&EN, May 8, page 35) was even more biased and self-serving. He marshals three arguments to support his contention that the dangers of pesticides are minimal and are far outweighed by their benefits. (1) "For almost every pesticide, the dietary intake is less than 1% of the acceptable daily intake defined by toxicologists." I have two problems here: One is the "almost" (what of the others); and second, Hol-

Correction

• June 19, page 98: In the Committee on Professional Training table, the data for chemistry graduates from the University of Washington and Wayne State University were transposed. Therefore, the tables on page 99 should have Washington as 17th in the ranking of producers of bachelor graduates, with 50, and Wayne State as 23rd, with 45. For certified bachelor graduates, Washington, not Wayne State, ranked seventh with 37. For masters graduates, Washington ranked eighth with 17, and Wayne State 20th with 14. For Ph.D.s, Washington, not Wayne State, ranked 25th with 22. Also, Washington, not Wayne State, was the only school apart from the University of Illinois, Urbana-Champaign, to appear in all four rankings.

Producers, Users Grapple with Realities of CFC Phaseout

First cap on chlorofluorocarbon production went into effect on July 1, with timetable for phaseout still being debated, U.S. producers facing possible windfall profits tax, and state and local regulations proliferating

Pamela S. Zurer, C&EN Washington

For the chlorofluorocarbon (CFC) industry, nothing is certain these days but death and taxes. The business of producing CFCs is doomed—the only question is how quickly the end will come. And the Bush Administration is determined to impose a windfall profits tax on the makers of CFCs as production of the chemicals is cut back.

But surrounding those harsh realities are many uncertainties. The timetable for phasing out the ozone-depleting chemicals is still being debated, both in the international arena and among U.S. policymakers. Within the U.S., state governments are adding their own restrictions to those already imposed by the federal Environmental Protection Agency (EPA).

The chemicals, processes, and technologies that will replace CFCs in their myriad uses are still being identified. One of the industries that uses CFCs, rigid foam insulation, fears for its life. Many others, ranging from the electronics industry to automobile manufacturing, are shaken by the need to forego CFCs. And the most likely chemical substitutes—chlorofluorocarbons that bear hydrogen atoms (HCFCs)—may themselves end up being regulated as potential ozone depleters.

On July 1, the first restrictions on the manufacture of fully halogenated CFCs went into effect. Producers were required to freeze their output of the chemicals at 1986 levels. That production cap—required under the terms of the Montreal Protocol on Substances That Deplete the Ozone Layer and by EPA regulations that implement that international treaty within the U.S.—is turning out to be a production cut of 15% or more, because output of CFCs has grown since 1986.

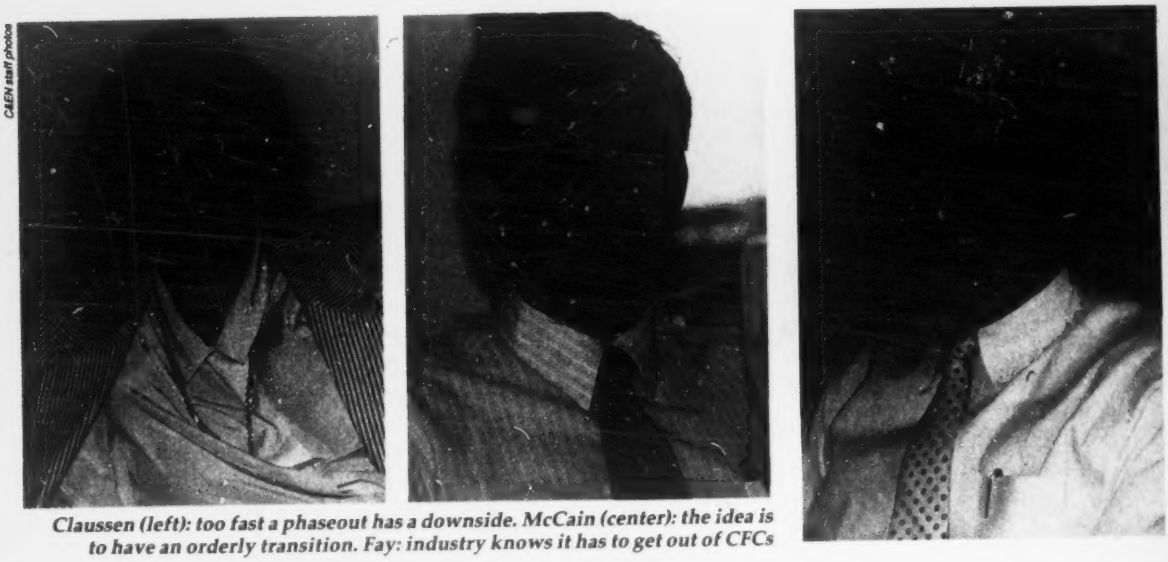
As they now stand, the Montreal protocol and EPA rules require that CFC production be reduced another 20% by mid-1993, then an additional 30% by mid-1998. Output of halons (fluorocarbons that contain bromine) is to be frozen at 1986 levels in 1992. EPA has set up a quota system that allocates future production of the controlled chemicals based on each U.S. producer's share of the 1986 market for halons.

Recycling of CFC-12 from automobile air conditioners could become mandatory under pending legislation

But the Montreal protocol was out of date even before it went into effect. Since it was negotiated in 1987, a flood of scientific data has indicated the treaty as currently written will not adequately protect the ozone layer from chlorine-catalyzed destruction. In the past two years the atmospheric science community has made three major findings:

- Chlorine and bromine from CFCs and halons are a primary factor in the seasonal loss of ozone at the South Pole known as the Antarctic "ozone hole"

C&EN staff photos



Claussen (left): too fast a phaseout has a downside. McCain (center): the idea is to have an orderly transition. Fay: industry knows it has to get out of CFCs

(C&EN, May 30, 1988, page 16). In the worst year to date, 1987, 50% of the ozone over Antarctica was destroyed during September and October.

• On a global basis, the ozone layer has shrunk an average of about 2.5% during the past decade, even after accounting for natural variability (C&EN, March 21, 1988, page 6).

• The winter atmosphere in the north polar region is loaded with the same destructive chlorine compounds that cause the Antarctic ozone hole. Although no massive loss of ozone has been observed in the Arctic, scientists participating in an international research program that probed the Arctic stratosphere last winter concluded the potential for significant change is there (C&EN, March 6, page 29).

The accumulation of bad news about the layer of ozone that protects Earth's surface from harmful ultraviolet (UV) radiation has led to a consensus that tighter controls on chemicals that carry halogen atoms into the stratosphere are necessary. If provisions set in the Montreal protocol were to be followed, chlorine concentrations would continue to increase for more than a century. Stricter controls on halogenated compounds are required simply to stabilize the chlorine content of the atmosphere at today's levels of about 3 ppb, much less reduce them below the concentrations—about 2.7 ppb—that existed when the Antarctic ozone hole was first identified in 1985.

Given the reality of the science, over the past 18 months industrial producers and users of CFCs—led by Du Pont, the company that makes about 25% of CFCs produced worldwide and dominates the U.S. market—have joined environmental groups, scientists, and politicians calling for a phaseout of CFCs.

"When the industry decided in 1986 to support an international agreement to limit the use of CFCs, it recognized that the long-term life of the current compounds was going to be limited," says Kevin J. Fay, executive director of the Alliance for Responsible CFC Policy. That industry group is a coalition of all five domestic CFC manufacturers and several hundred businesses that use CFCs.

"Now, based on science and the political climate of today, it's clear they are going to be a lot more limited than we thought the science justified in 1986," Fay says. "Back then it appeared that you only had to cap the growth in use of the compounds. I don't think anybody believes that anymore. Even under the Montreal protocol, you get substantial increases in chlorine concentrations in the atmosphere."

But the Montreal protocol soon will be strengthened. In Helsinki in early May, delegates to the first meeting of the countries that have joined the treaty agreed on their intention to phase out production and consumption of CFCs no later than the year 2000. They also agreed to eliminate halons and control other ozone-depleting substances like carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3) as soon as feasible (C&EN, June 26, page 33).

Four review panels set up by the United Nations Environment Program (UNEP) are now completing scientific, environmental, technical, and economic assessments of the issues surrounding these tighter controls. Once UNEP has received their reports, amendments to the Montreal protocol will be drafted this fall. A CFC phaseout is expected to be formally adopted next spring when the parties meet again to renegotiate the treaty.

However, although an eventual phaseout of CFCs now appears inevitable, the timing of their elimination is still being negotiated. The year 2000 is too late, according to some environmentalists and politicians. The most extreme position is that taken by Greenpeace, an international environmental group, which is calling for an immediate ban on all production and consumption of CFCs and halons. Others, while conced-

ing the need for some transition time, argue the phaseout must be speeded up. A new bill in the Senate, for example, calls for their elimination within five years.

"The 2000 date is not acceptable in our view," says Liz Cook, project director for the Friends of the Earth Foundation's (FOE's) ozone campaign. "That schedule is based on a timetable the chemical industry has set for itself. It doesn't force technological innovation."

Some Scandanavian countries have already committed themselves to phaseouts before 2000, Cook points out. Others, including the European Community, have pledged to cut CFC output 85% as soon as possible.

"The idea is to have an orderly transition over the next decade or so," argues C. Anthony McCain, program manager of Du Pont's Freon products division. "There will be immediate injuries to people if we move too fast, because they will not choose the best solutions. They'll be exposed to toxic, flammable materials."

EPA agrees that 2000 is soon enough. "Although some people have said they would like a phaseout faster than 2000, we don't believe there is much environmental benefit to doing it faster and there is a downside," says Eileen B. Claussen, director of the agency's office of atmospheric and indoor air programs. "You might pick poorer alternatives because they are available first."

The fate of halons is also uncertain. Although output of halons is small compared with CFCs, bromine derived from those compounds is even more destructive to stratospheric ozone than chlorine. The U.S. and some other countries have called for an international phaseout of halons by 2000, but the extent and timing of further controls remains to be negotiated.

Carbon tetrachloride and methyl chloroform are also in limbo. EPA argued forcefully at the Helsinki meeting that both could be significant future sources of chlorine in the stratosphere if their output is allowed to grow unchecked.

Carbon tetrachloride is used primarily as a chemical intermediate in the U.S., but Soviet bloc and developing countries use it in ways that allow emissions to the atmosphere, according to Claussen. As for methyl chloroform, EPA fears that manufacturers will use it as a substitute for other solvents—primarily CFC-113 ($C_2Cl_3F_3$)—that have been restricted.

"I am sure that both carbon tet and methyl chloroform will end up in the renegotiation" of the Montreal protocol, Claussen says. "But whether they end up at a freeze or some reduction I don't know yet. Technically, if you want to stabilize chlorine in the atmosphere—which is not necessarily a wonderful environmental goal—you probably have to do away with both of them over some period of time."

Meanwhile, prices of CFCs have already begun to rise as the supply shrinks under the current restrictions—from about 60 and 70 cents per lb for CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) a year ago to approximately 80 and 90 cents per lb today. EPA estimates prices may eventually rise as much as fivefold, bringing producers several billion extra dollars, depending on how fast users switch to substitute products or alternative technologies.

"The government is restricting the supply of CFCs for a good environmental reason," says attorney David D. Doniger, director of the Natural Resources Defense Council's ozone protection project. "The effect is the same as the OPEC cartel's oil restrictions' effect on oil prices. If the price goes up but the production costs don't, that's pure windfall profit."

Almost a year ago, EPA floated the idea of imposing a regulatory fee on CFC producers or an auction system to recoup those additional revenues. Otherwise, the agency suggested, CFC producers might lack the incentive to come up with substitutes.

EPA still has not taken any action. But the Bush Administration has included $400 million in CFC windfall profits revenue in its proposed fiscal 1990 federal budget and is projecting another $1.4 billion for the following year—much to the fury of CFC producers.

"This is definitely inappropriate," says Anthony Vogelsberg, environmental manager of Du Pont's Freon products division. "The scheme would extract the very revenues necessary to do the research and development work necessary to replace CFCs."

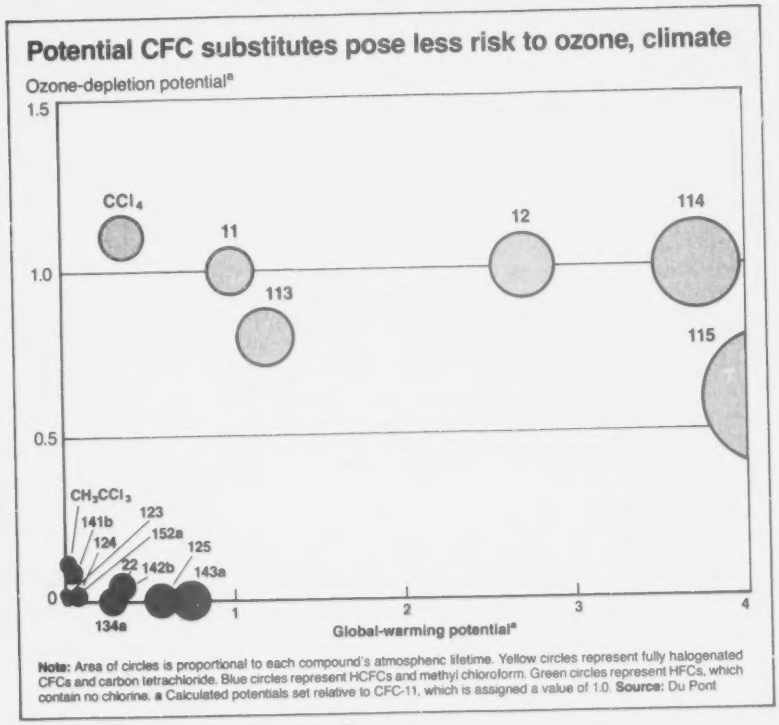
Such a tax would also place U.S. companies at a competitive disadvantage, argues William Corcoran, director of public affairs for Allied-Signal, the second largest U.S. CFC producer. "The American companies are doing a good job with moving ahead with alternatives," he says. "Now we'll be hit with a big tax—which no other country imposes—that makes it tougher for us to maintain our lead."

However, that view hasn't garnered a lot of sympa-

Eight halocarbons are controlled under Montreal protocol

Substance	Ozone-depletion potential[a]	Atmospheric lifetime, years	Major uses
GROUP 1—Production cuts mandated			
CCl_3F (CFC-11)	1.0	75	Flexible foam, rigid polyurethane foam, refrigeration, air-conditioning
CCl_2F_2 (CFC-12)	1.0	111	Rigid polyurethane and rigid nonpolyurethane foam, refrigeration, air-conditioning, aerosols, sterilization, food-freezing
$C_2Cl_3F_3$ (CFC-113)	0.8	90	Solvent
$C_2Cl_2F_4$ (CFC-114)	1.0	185	Rigid nonurethane foam, refrigeration, air-conditioning
C_2ClF_5 (CFC-115)	0.6	380	Refrigeration, air-conditioning
GROUP 2—Production freeze mandated			
$CBrClF_2$ (Halon-1211)	3.0	25	Portable fire extinguishers
$CBrF_3$ (Halon-1301)	10.0	110	Total flooding fire-extinguishing systems
$C_2Br_2F_4$ (Halon-2402)	6.0	na	Fire extinguishers

a Estimates depending on chlorine and bromine content and atmospheric lifetime. Potentials are set relative to CFC-11, which is assigned a value of 1.0. **na** = not available. **Source:** Environmental Protection Agency



Note: Area of circles is proportional to each compound's atmospheric lifetime. Yellow circles represent fully halogenated CFCs and carbon tetrachloride. Blue circles represent HCFCs and methyl chloroform. Green circles represent HFCs, which contain no chlorine. a Calculated potentials set relative to CFC-11, which is assigned a value of 1.0. **Source:** Du Pont

thy in some quarters. "There are no entities who deserve the windfall less than the CFC producers that stonewalled this issue for so long and got us into this mess," NRDC's Doniger says. "So we are in favor of the windfall profits mechanism to take those profits away. We're encouraged by EPA's discussion and even more encouraged by the Bush Administration's inclusion of the money in the budget."

Congress, not EPA, looks likely to make the final decision on the issue. Although EPA is careful to refer to potential CFC windfall revenues as "fees," they bear a strong resemblance to taxes—which only Congress can impose. The Justice Department says EPA has the authority to implement a fee or auction system under the Clean Air Act. But the General Accounting Office noted in the recent study that EPA will undoubtedly be sued if it does.

But it probably won't come to a lawsuit. The Senate Environment & Public Works Committee has embraced CFC taxes as a way to come up with most of the $450 million it has orders to slash from the fiscal 1990 budget. The committee is leaning toward a tax on each pound of CFCs and halons produced, with the amount increasing each year until the compounds are phased out.

Although the final budget won't be enacted until fall, CFC producers are facing the likely reality of having to pay a windfall profits tax. "In order to get that money we would have to triple the prices of CFCs next year," Du Pont's McCain says bluntly. "If we have to pay that money we will pass that cost on to the user. He'll pay for it and we'll pass it on to the government for him. Some users will go out of business."

The CFC users that will suffer the most as supplies become short and prices rise are makers of rigid insulating foam. CFC-11 is used to blow the polyurethane and polyisocyanate foam insulation widely used in new construction and remodeling. The CFCs not only mechanically expand the foams, but are trapped within them, contributing to their insulating capacity.

The foams already face stiff competition from other types of insulation, such as glass fiber, notes Stephen O. Anderson, chief of EPA's technology and economics branch in the division of global change. "They face a fragile market because there are so many other good alternatives," he says.

The foam insulation industry is evaluating HCFCs-123 ($CHCl_2CF_3$) and -141b (CH_3CCl_2F) as substitutes for CFC-11. But these compounds are still undergoing long-term toxicity testing and process development and are not yet available in commercial quantities. Du Pont recently announced plans to build a commercial-scale plant for HCFC-123 in Maitland, Ontario, but it won't be able to sell any until 1991 at the earliest, and then only if everything goes right. "We're taking a significant financial risk to try to get material out to our customers," McCain says.

In any case, the HCFCs will cost several times what CFCs now cost—perhaps too expensive for foams to compete with other types of insulation. If a windfall profits tax is imposed on the current CFCs, the industry argues, foam insulation makers will be out of business that much sooner.

The auto industry is fighting additional restrictions on CFCs on a different front—the state level. In May, the Vermont legislature outlawed the registration of cars with air conditioners that use CFCs beginning with 1993 models. California's lawmakers may soon follow suit. A bill just introduced in the U.S. Senate would make it illegal to sell or export cars that use CFCs in their air conditioners after 1993.

U.S. carmakers say they can't make the 1993 deadline. "We may not have any cars that use the substitutes by the '93 auto year," says General Motors' Gerald F. Stofflet, chairman of the Motor Vehicles Manufacturers Association's CFC subcommittee.

About 90% of the new cars sold in the U.S. have air conditioners. All use CFC-12. Automakers in the U.S., Europe, and Japan are testing new systems that use HFC-134a (CH_2FCF_3), which contains no chlorine atoms. Both Du Pont and ICI are working on commercial-scale plants to produce HFC-134a, which

C&EN staff photos

Doniger (left): a balanced position is available. Anderson: foams face a fragile market

also has potential uses in home and commercial refrigeration. But as is the case with the HCFCs, toxicity tests and process development on HFC-134a won't be completed for several years. Furthermore, as Du Pont's McCain points out, HFC-134a is not a "drop-in" replacement for CFC-12.

"Everybody's working, trying to get HFC-134a in, but there are still many uncertainties," Stofflet says. "We release the 1993 models for tooling at the end of this year and trying to put in a different system after that is a disaster. The earliest we can do it is the 1994 model year."

Even then, Stofflet says, the auto companies will be taking a big risk because they will have to finalize their designs before all testing is complete. And the new air-conditioning systems require so many changes throughout the cars that the companies will not be able to put them in all models at once, he says, but will have to phase them in over three or four years.

The headache that the automakers are facing stems from an outpouring of legislation pending at the state and local level that restrict CFCs. "We're running around putting out fires," Stofflet says. "It's a real problem. Each state proposes something a little bit different."

Not all the proposed legislation involves the auto restrictions that Vermont's does. Instead, most proposed bills are more like one recently enacted in Hawaii, which requires recycling of CFC-12 when auto air conditioners are serviced and bans the sale of small cans of the refrigerant for home use. Other pending bills would require labeling of products that contain or are made with CFCs.

All this legislation—some 90 bills in more than 20 states this spring—is a result of EPA's decision that its federal regulations controlling production of CFCs do not preempt the rights of states and municipalities to enact their own restrictions on the chemicals. CFC producers and users are most unhappy with that decision—and environmental groups are taking full advantage of it.

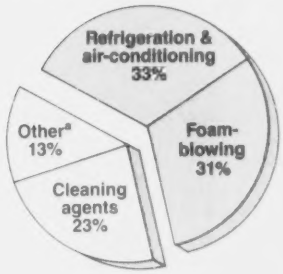
"It would be disingenuous for me to pretend that we are not aware that it can be inconvenient to companies who want uniform national markets," NRDC's Doniger says. "So our strategy is to promote this state-level action. But I don't want people to think we can turn it on or off. A lot of it is indigenous. The activity reflects real concern at a grass-roots level that the global process and the U.S. federal process are working too slowly."

"We don't need these state and local initiatives to persuade the industry that we have to get out of these compounds," Fay says. "We know that. States and localities would be far better off finding where they use CFCs and putting their own ozone protection programs into place rather than trying to ban the registrations of auto air-conditioning systems or banning individual products. That is not going to affect the total amount of CFC use in this country because we are going to be in a shortage situation governed by the Montreal protocol. All these individual efforts to try to ban a product here or a product there are not going to accomplish anything."

But according to environmentalists who have been involved in state initiatives, the goal of the bills is not just to tighten supplies of CFCs. It is to restrict needless emissions and conserve CFCs for essential uses like servicing existing refrigeration equipment.

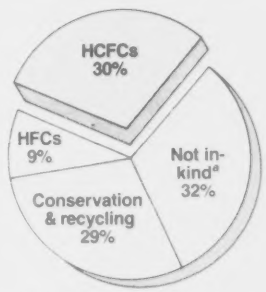
"We're working with states on banning frivolous uses and on mandatory recycling for auto air-conditioning," FOE's Cook says. She points out that releases of CFC-12 from car and truck air con-

Cooling, foam-blowing dominate U.S. CFC uses



a Includes aerosols, sterilization, and other miscellaneous uses. **Source:** Alliance for Responsible CFC Policy

HCFCs will fill 30% of demand for CFCs in 2000



Note: Estimates are projections of how market demand now satisfied by CFCs will be met in 2000. a Alternative products or technologies. **Source:** Du Pont

Many routes lead to hydrogen-bearing alternatives to CFCs

The very stability of fully halogenated CFCs that makes them so useful is the same characteristic that renders them dangerous to the stratospheric ozone layer. Because they are so unreactive, essentially all CFC molecules that are emitted in the lower atmosphere eventually diffuse into the stratosphere. The intense ultraviolet radiation there liberates chlorine atoms that then can catalyze reactions that destroy ozone molecules.

In contrast, hydrogen atoms on the leading candidates to replace the fully halogenated CFCs—hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs)—make them susceptible to degradation in the lower atmosphere, before they can reach the stratosphere. But those same hydrogen atoms that make the alternative compounds less destructive to ozone make them more difficult and thus more costly to prepare.

It's easy to make the fully halogenated compounds. To prepare CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2), carbon tetrachloride (CCl_4) is mixed with hydrogen fluoride (HF) in the presence of a catalyst. The temperature and pressure in the reactor control how many chlorine atoms are exchanged for fluorine: one exchange gives CFC-11; two exchanges CFC-12.

C&EN staff photo

Manzer: a chance for a global impact

The key to developing alternatives, says Leo E. Manzer, research manager at Du Pont's experimental station in Wilmington, is to match the physical properties of the CFCs being replaced. "There's an estimated $135 billion worth of equipment in the U.S. that uses CFCs," he says. "Clearly you can't ask everybody to scrap their old equipment, then redesign, rebuild, and put in all new equipment. You've got to find something that comes close to the existing compounds."

But to add hydrogen atoms to ensure the compounds are oxidized in the troposphere and at the same time get a close match in physical properties means turning to compounds that contain two carbon atoms, Manzer says. "If you replace chlorine in CFC-11 or -12 with a hydrogen, your boiling points are far too low," he says, "so you have to put a little more weight in the molecule by going to a two-carbon molecule."

Working with two-carbon fragments, however, adds the complexity of dealing with isomers. And there are a wide variety of reaction routes, starting from a number of possible materials, to the desired replacements. Each conceivable route has different problems associated

ditioners are currently the largest single source of CFC emissions in the U.S.

Technology for recycling CFC-12 from auto air conditioners is available now, says EPA's Anderson. Earlier this year, EPA and major auto manufacturers announced an agreement on standards of purity for recycled CFC-12 that will allow mechanics to reuse the old refrigerant without voiding the air conditioner warranty (C&EN, Feb. 6, page 6).

"I can understand how industries who make products they'd like to sell in nationwide markets are concerned about labeling requirements and restrictions and so forth that have popped up at the state level," Doniger says. "The most efficient answer to that, though, is for them to come to Washington and support national control measures. If we had a national auto recycling law, we wouldn't need to have 50 state recycling laws. If we had national labeling requirements, we wouldn't need inconsistent state labeling requirements."

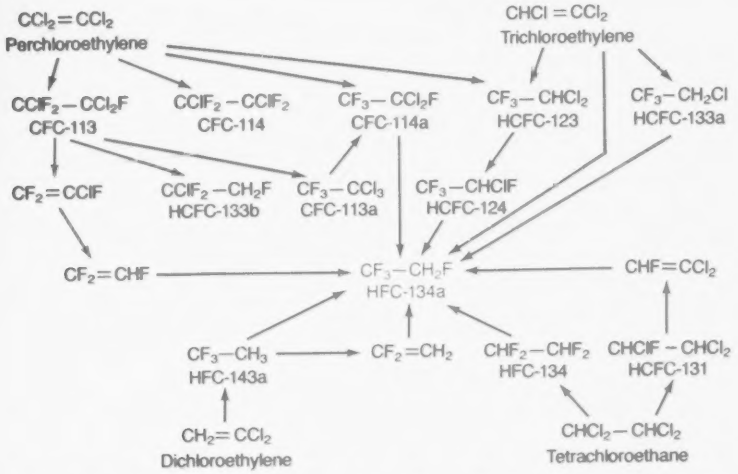
EPA's Claussen says that the agency has no plans to initiate such national regulations on its own. She would, however, look into it if asked to by the industries affected.

Claussen also asserts that EPA has no plans to restrict the use of HCFCs, although some politicians and environmentalists are calling for controls. CFC producers have been concentrating on developing HCFCs and HFCs as substitutes for the fully halogenated compounds. And the current refrigerant of choice for home air-conditioning in the U.S. is HCFC-22 ($CHClF_2$).

The hydrogen atoms on HCFCs make them susceptible to oxidation in the lower atmosphere. But some fraction reaches the stratosphere where UV radiation can release chlorine atoms that catalyze ozone destruction.

"I think in the end you have to be practical," Claussen says. "It is more important to get out of CFCs by some date certain than to regulate the HCFCs. And you need the HCFCs, for at least some CFC uses, in order to do that. If you use HCFCs wisely and not that much, it is probably okay. But I don't want to specify in a regulation how much is wisely, or what uses. On the other hand, I want to monitor exactly how much is being produced and what it is being used for, on a worldwide basis."

But pressures are mounting for restrictions on the future output of HCFCs. In the international arena, there was limited discussion at the May Helsinki meeting of whether HCFCs should be included in the renegotiations of the Montreal protocol. In the U.S., a draft bill, circulating in the Senate, would limit the time period over which HCFCs could be used. At the extreme, Greenpeace has called for banning all production and new consumption of HCFCs. And both NRDC and FOE hold that future limits on HCFCs must be spelled out now.



with it. Each has to be explored if the best process is to be found.

"For example, look at HFC-134a (CF_3CH_2F)," Manzer suggests. "You can imagine starting from several different chlorinated feedstocks—Perclene ($CCl_2 = CCl_2$) or Tri-Clene ($CHCl = CCl_2$). Then look at the number of reactions that have to take place as you add fluorine and go through various intermediates. You've got a real nightmare on your hands. Separating these materials is really what gets us into difficulty from a process development standpoint."

Manzer points out another problem. Hydrogen fluoride, which is present in the addition and exchange reactions en route to the substitutes, tends to form unpredictable, hard-to-manage azeotropes with many fluorocarbons.

"The HCFCs and HFCs are a problem too from a catalyst standpoint," Manzer says. "They are less stable in the lower atmosphere, which is why they are acceptable as substitutes. But they are also less stable on catalyst surfaces. For example, when you have hydrogen in a two-carbon fragment you can eliminate HF or HCl. A significant amount of that takes place on some catalyst surfaces. That creates a real headache for many of us in the development effort, because the resulting olefins are toxic and you've got to remove them from the final product."

Despite the complexities involved in developing processes that can be commercialized, Manzer says his staff of chemists and chemical engineers are highly motivated and excited by their work. "It's not everybody that has a chance to have an impact on the entire world," he says. "Normally within an R&D organization it may take 10, 15, or 20 years before your catalyst research ever gets commercialized. Now we are talking about commercial plants within two or three years after we have done the chemistry. That is very satisfying."

"These chemicals are useful because if you use them now you can get rid of the hard CFCs that much sooner," Doniger says. "But we want to make sure we don't have topsy-turvy growth that slows down or even prevents the reduction of atmospheric chlorine levels and contributes to global warming."

Doniger says that before 1986 there was not much development work on HCFCs and HFCs. Until it was clear that restrictions would be placed on the existing CFCs, companies had no incentives to invest in more expensive alternatives. "As we put HCFCs into service we ought to continue the research—both from chemical companies and users—into other ways of getting the job done with less and less of those chemicals and ultimately none at all," he says. "If you create the false impression that HCFCs have an unlimited future, there will be no interest in working on a better answer."

But the idea of a limited future is causing the chemical companies to balk. "We are very disturbed by the regulatory uncertainty," says Allied-Signal's Corcoran. "We plan to produce a full line of substitutes. But when we get to the point where the management committee has to approve plans for large-scale investments—a quarter of a billion dollars over a decade—if these kinds of restrictions go through it will be much harder to justify."

Du Pont's McCain adds: "We have not decided to go forward in the alternatives business. We are making small-scale plants. But if in a few years, when we have to get authorization for world-scale production facilities, we don't anticipate we can make money, we won't do it. Faced with potential regulations like that, why would any reasonable businessperson want to invest in something that would have a short lifetime?"

Doniger suggests that a balanced position in the middle is available. Industry, he argues, should work toward a regulation that would allow companies enough time to recoup their investments and then get out of the business. "At least they'd know that the cloud over those chemicals isn't going to result in the rug being pulled out from under them two, three, or four years down the road," he says.

In the meantime, the uncertainty continues. For the moment it is limited to companies that produce and use CFCs and that are trying to plan for the future. But it will not be long before the effects of limited supplies of CFCs extend to the consumer.

"I don't think people have any idea of the impact this is going to have over the next few years," says Leo E. Manzer, research manager at Du Pont's central research and development department. "It's not going to be until people can't get their air conditioners charged up and have to suffer in the kind of weather we've had in the last few weeks that they'll realize how important CFCs are in all aspects of life." □